

## **PATTERNING MAGNETIC NANOSTRUCTURES**

### **RELATED APPLICATIONS**

This application claims benefit to provisional application 60/410,952 filed September 17, 2002 to Mirkin et al, the complete disclosure of which is hereby incorporated by reference in its entirety.

### **STATEMENT OF FEDERAL GOVERNMENT RESEARCH SUPPORT**

The subject matter of this application was developed in part with federal government funds from grant no. \_\_\_\_\_ from the Department of \_\_\_\_\_. The federal government may have certain rights in the invention.

### **BACKGROUND**

Magnetic materials are commercially important, and a commercial need exists to develop smaller magnetic structures, approaching single domain sizes. Processing of magnetic materials, however, can be a challenge, particularly at smaller scales. For example, high temperature may be needed for fabrication which could prevent some applications or increase production cost. Hence, a commercial need exists to find better methods to fabricate smaller magnetic structures. In addition, a commercial need exists to better understand how magnetic behavior is a function of structure size. For example, the coercivity of small particles can depend on particle size. At smaller sizes, moreover, interfacial surface effects generally become more significant. Layering of magnetic structures can be significant,

including the GMR effect (giant magnetoresistance effect). Many applications are important for small magnetic structures including high-density recording media, nonvolatile memories, microwave circuits, biosensors, bioelectronics, communication devices, and magnetic microscopy.

Types of magnets include soft magnets and hard magnets. In particular, hard magnets are of commercial interest which generally have high permanent magnetization, high coercivity (e.g.,  $H_c$  greater than or equal to about 10 Oe), and high mechanical and chemical stability. Generally, hard magnets, which are a type of permanent magnet, display a relatively squarish magnetization v. field (M-H) loop, coupled with physical and chemical stability. For example, they can be useful permanent magnets which are difficult to demagnetize by unexpected fields. One important example of a hard magnet is barium hexaferrite (BaFe). Like many magnetic materials, however, BaFe, can be difficult to pattern at higher resolution. Thin film preparation can be carried out using rf sputtering, or reactive magnetron sputtering, followed by annealing at high temperature. Some of the resultant thin film can be nonmagnetic. In addition, a need exists to reduce the grain size.

Small magnetic structures, in principle at least, can be patterned by electron beam lithography, but this method requires expensive instrumentation and is not very versatile. For example, the electron beam can introduce chemical changes to the materials upon exposure and requires a high vacuum.

Improved methods are needed to pattern small magnetic structures including nanostructures. The methods should be convenient, versatile, and provide high resolution and alignment. Methods should be applicable to magnetic materials which are difficult to process.

## SUMMARY

The present invention provides multiple embodiments, and this summary of these multiple embodiments should not be used to limit the scope of the invention.

For example, in one embodiment, the present invention provides a method of forming a magnetic nanostructure comprising: depositing a magnetic nanostructure precursor on a substrate from a nanoscopic tip; and converting the precursor to form the magnetic nanostructure on the substrate.

For example, in another embodiment, the present invention provides a method of forming a hard magnet nanostructure comprising: depositing a hard magnet nanostructure precursor on a substrate from a tip; and converting the precursor to form the hard magnet nanostructure on the substrate.

The present invention also provides a method of forming a soft magnet nanostructure comprising: depositing a soft magnet nanostructure precursor on a substrate from a tip; and converting the precursor to form the soft magnet nanostructure on the substrate.

The present invention also provides a method of forming a sol gel magnetic nanostructure comprising: depositing a sol gel magnetic nanostructure precursor on a substrate from a tip; and converting the precursor to form the sol-gel magnetic nanostructure on the substrate.

The present invention also provides a method of forming an array of magnetic nanostructures comprising: depositing one or more magnetic nanostructure sol-gel precursor on a substrate to form a plurality of nanostructures of precursors; and converting the nanostructures to form the array of magnetic nanostructures.

The present invention also provides a method of forming a ferromagnetic nanostructure comprising: depositing a ferromagnetic nanostructure precursor on a substrate; and converting the precursor to form the ferromagnetic nanostructure on the substrate,

wherein the precursor comprises a solvent based patterning ink consisting essentially of magnetic precursor and solvent in sol state.

The present invention also provides a method of nanolithography comprising: providing a substrate, providing a nanoscopic tip having an inking composition thereon, wherein the inking composition comprises at least one magnetic material precursor; transferring the inking composition from the nanoscopic tip to the substrate to form a deposit on the substrate comprising at least one magnetic material precursor.

The present invention also provides a method of nanolithography comprising: positioning a scanning probe microscopic tip having a magnetic reactive ink composition thereon relative to a substrate so that the reactive ink composition is transferred from the nanoscopic tip to the substrate to form a deposit on the substrate, wherein the reactive ink is a sol-gel precursor capable of undergoing a sol-gel reaction.

The present invention also provides a magnetic nanostructure comprising a substrate and one or more magnetic nanostructures disposed thereon, wherein the nanostructure has a lateral area of about  $100,000 \text{ nm}^2$  or less.

The present invention also provides an array of individual magnetic nanostructures comprising: a substrate and individual magnetic nanostructures disposed thereon, wherein the nanostructure has a lateral area of about  $100,000 \text{ nm}^2$  or less.

The present invention also includes articles made from these methods and uses of the methods. Basic and novel features of the invention include use of relatively inexpensive instrumentation, good alignment and resolution, and versatility in compositions which can be deposited under controlled conditions, and ability to deposit and image with the same instrument. Ink compositions can be formulated to exclude components which interference with the deposition process, be they solvent or large magnetic particles.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 provides a schematic diagram depicting the patterning of magnetic BaFe nanostructures on silicon oxide. (a) An atomic force microscope (AFM) tip coated with a precursor solution of barium ferrite is brought into contact with the silicon oxide substrate. (b) The solution is transferred to the substrate as the tip is traversed across it. (c) Post-annealing yields the desired BaFe nanostructures.

Figure 2 provides characterization of the bulk BaFe particle samples. (a) XRD pattern of as-synthesized BaFe particles. The indexing is based on tabulated hexagonal  $\text{BaFe}_{12}\text{O}_{19}$  reflections. (b) XRD spectrum of BaFe particles synthesized without the preheating step. (c) Transmission electron microscope (TEM) image of as-synthesized BaFe particles. (d) High resolution TEM image showing single crystal nature of these particles. (e) Energy-dispersive x-ray spectroscopy (EDXS) spectrum obtained from these nanoparticles. The signal for Cu comes from the copper grid on which these particles were supported. (f) Magnetic hysteresis measurements of the particles at room temperature.

Figure 3 provides scanning probe microscope (SPM) studies of the BaFe pattern and x-ray photoelectron spectroscopy (XPS) characterization. (a) Topographic AFM image of magnetic BaFe lines on the silicon oxide substrate. The speed for the BaFe precursor deposition is  $0.2\text{ }\mu\text{m/s}$ . (b) Topographic AFM image of an array of magnetic bars. The deposition speed is  $0.1\text{ }\mu\text{m/s}$ . (c) Cross-sectional topography trace of a line (marked by the arrows in b). (d) Magnetic force microscope (MFM) image obtained from these magnetic bars. (e) Barium peaks were detected from the silicon oxide substrate using XPS. (f) Iron peaks detected from the same sample (inset: oxygen peaks and the deconvolution result).

Figure 4 provides an AFM image of DPN patterning of manganese ferrite ( $\text{MnFe}_2\text{O}_4$ ) nanostructures. The distance between the centers of the nanostructures is about 400 nm. The dot size is about 150 nm.

#### DETAILED DESCRIPTION

The complete disclosure of priority provisional application 60/410,952 filed September 17, 2002 to Mirkin et al, is hereby incorporated by reference in its entirety including the figures, description, and claims.

In addition, the complete disclosure, including the figures, of the following paper to Fu et al. is incorporated by reference: "Nanopatterning of 'Hard' Magnetic Nanostructures via Dip-Pen Nanolithography and a Sol-Based Ink," *NanoLetters*, 2003, Vol. 3, No. 6 757-760.

One skilled in the art can refer to the technical literature in practicing the present invention including literature on magnetic materials, sol-gel processing, and nanolithographic printing including DPN printing. In particular, one skilled in the art can refer to the technical literature for assistance in the practice of the claimed invention, which relates to magnetic materials, and in particular, magnetic materials comprising metals and metal oxides. For example, magnetic materials in information storage technology are described in P. Ball, *Made to Measure: New Materials for the 21<sup>st</sup> Century*, Princeton, Chapter 2, pages 63-102, 1997; and C.P. Poole and F.J. Owens, *Introduction to Nanotechnology*, Chapter 7, "Nanostructured Ferromagnetism," pages 165-193, 2003, Wiley. See, also, J. Shackelford, *Introduction to Materials Science for Engineers*, 4<sup>th</sup> ed., Prentice Hall, 1996, in particular

chapter 13, pages 502-530. Recently, there has been considerable interest in methods for synthesizing and patterning magnetic small scale, microscale, and nanoscale materials and related ceramic and conductive materials. In addition to exhibiting novel size-dependent properties (see documents 1-10, for example), these materials (particularly ones with high coercivities and mechanical stabilities, e.g., semi-hard and hard magnets) are being explored as potential avenues to high-density recording media (see documents 11-14, for example). All of the references described in this paragraph are incorporated herein by reference.

In the present invention, patterns of magnetic materials can be formed by lithography and related deposition fabrication methods providing small structures including nanostructures at high resolution. The magnetic material formed by patterning, and if necessary subsequent post-patterning treatment, is not particularly limited. In general, the sol-gel process route to magnetic material formation can be used, and magnetic materials which are compatible with the sol-gel route can be used. Commercially important metallic magnets for the present invention can be ferromagnetic. Further, these materials can be generally categorized as either soft, semi-hard, or hard magnets. In general, the compositional and structural factors that lead to magnetic hardness are generally the same ones that produce mechanical hardness, as described in, for example, J. F. Shackelford, *Introduction to Materials Science for Engineers*, 4<sup>th</sup> Ed., 1996, including chapters 7 and 13. In addition, another type of magnetic material includes ceramic magnets.

Hard magnets can be used in permanent magnet applications. Examples of hard magnet alloys include samarium-cobalt, platinum-cobalt, and Alnico. The hard magnet of the present invention, however, is not particularly limited. Ba/Sr hexaferrites can be used. Barium hexa-ferrite (for purposes of this disclosure, "BaFe,"; ideal chemical formula representation is  $\text{BaFe}_{12}\text{O}_{19}$ ), in particular, is a good hard magnet candidate for such media, but it is challenging to achieve high resolution patterning of BaFe by conventional

lithography and etching processes (see documents 15, 16, for example). BaFe is a permanent magnet with large magnetic anisotropy. The BaFe compositions of the present invention can further comprise impurities and can be used as mixtures, although in general it is preferred that the BaFe composition is at least 50% by weight pure BaFe, and more preferably, at least 80% by weight pure BaFe. For example, strontium and calcium ferrites can be impurities in barium ferrite.

Besides BaFe and analogs thereof such as for example  $\text{SrFe}_{12}\text{O}_{19}$ , other examples of hard magnets include hexagonal ferrites, as well as compounds/alloys including, for example,  $\text{SmCo}_5$ ,  $\text{Sm}_2\text{Co}_{17}$ ,  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , and other ferromagnetic oxides and ferromagnetic compounds/alloys.

Barium ferrite and related compositions, including their preparation methods, are known in the art as in, for example, US Patent Nos. 4,042,516; 4,277,552; 4,407,721; and 4,582,623.

Preferred embodiments of the present invention comprise hard magnetic materials, and magnetic materials which can be fabricated and generally processed by sol-gel methods, and can be generally fabricated into small patterns with use of nanolithography and printing inks.

Herein, a novel direct-write nanopatterning method for a variety of magnetic materials, including hard magnets and BaFe, is disclosed, based upon DIP PEN NANOLITHOGRAPHY™ printing (DPN™ printing) and also based on a sol-gel process. DIP PEN NANOLITHOGRAPHY™ and DPN™ are trademarks of NanoInk, Chicago, IL and are used accordingly herein. Instrumentation and equipment related to this nanolithographic method can be obtained from NanoInk. Generally, although nanolithography and nanostructures are preferred in the present invention, microlithography and microstructures can be also carried out by the DPN printing method. Applications for



nanolithography and magnetic materials are described in, for example, US Patent Nos. 5,461,600 (Pohl, Oct. 24, 1995); 5,772,405 (Chou, June 30, 1998); and 6,519,221 (Manalis, February 11, 2003).

Nanolithography, including DPN printing, can be used to practice the present invention, particularly methods involving deposition or transfer of materials from a tip such as a nanoscopic tip to a substrate. For example, in patent application 09/866,533, filed May 24, 2001, (U.S. patent publication no. US 2002/0063212 A1 published May 30, 2002 to Mirkin et al.) DPN printing background and procedures are described in detail covering a wide variety of embodiments including, for example:

- background (pages 1-3);
- summary (pages 3-4);
- brief description of drawings (pages 4-10);
- use of scanning probe microscope tips (pages 10-12);
- substrates (pages 12-13) including magnetic substrates;
- patterning compounds (pages 13-17);
- practicing methods including, for example, coating tips (pages 18-20);
- instrumentation including nanoplotter (pages 20-24);
- use of multiple layers and related printing and lithographic methods (pages 24-26);
- resolution (pages 26-27);
- arrays and combinatorial arrays (pages 27-30);
- software and calibration (pages 30-35; 68-70);
- kits and other articles including tips coated with hydrophobic compounds (pages 35-37);
- working examples (pages 38-67);
- corresponding claims and abstract (pages 71-82); and

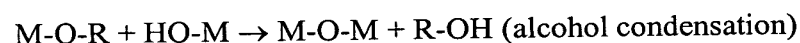
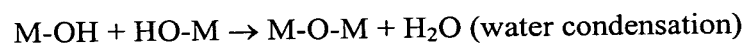
- figures 1-28.

All of the above document text, including each of the various subsections enumerated above including the figures, is hereby incorporated by reference in its entirety and form part of the present disclosure, supporting the claims.

In combination with direct write printing, sol-gel chemistry can be used to practice the present invention, and one skilled in the art can refer to the literature regarding sol-gel processing, particularly as it relates to magnetic applications: U.S. Pat. No. 5,545,432, for example, to DeGuire et al. (Aug. 13, 1996) describes sol gel process of metal oxide films including magnetic material films. For example, microstructures, nanostructures, microarrays, and nanoarrays can be prepared using the technologies of sol-gel chemistry and DPN printing in combination. For the present invention, the sol-gel process generally refers to a low temperature method using chemical precursors that can produce solid state structures such as magnetic materials, ceramics and glasses with better purity and homogeneity than high temperature conventional processes. This process can be used to produce a wide range of compositions (for example metal oxides) in various forms, including compositions useful for powders, fibers, coatings/thin films, monoliths, composites, and porous membranes. In the present invention, organic/inorganic hybrids, where an inorganic gel is impregnated with organic components such as polymers or organic dyes to provide specific properties, can also be made. An attractive feature of the sol-gel process is the capability to produce compositions not possible with conventional methods. Another benefit is that the mixing level of the solution is retained in the final product, often on the molecular scale. For example, nanocomposites can be made. Applications for sol-gel derived products, including those of the present invention, are numerous and include the magnetic applications described herein. Applications include coatings and thin films used in electronic, optical and electro-

optical components and devices, including optical absorption or index-graded antireflective coatings. Other example devices include capacitors, memory devices, substrates and infrared (IR) detectors. Additional devices include thin film transistors, field effect transistors, bipolar junction transistors, hybrid transistors, charge transfer devices, field emission devices, integrated circuits, solar cells, light emitting diodes, flat panel displays, optical waveguides, and waveguide division multiplexers. Antireflection coatings are also used for automotive and architectural applications. Magnetic materials can be also used in life sciences, pharmaceuticals, diagnostics, and sensors. U.S. Pat. No. 6,326,087 describes sol-gel processing to form metal oxide films for magnetic applications, and is incorporated herein by reference.

For purposes of the present invention, the sol-gel process can be carried out in liquid solution of organometallic precursors, which, by means of hydrolysis and condensation reactions, lead to the formation of a new phase (sol).



The sol can be made of solid particles suspended in a liquid phase. Then the particles can condense in a new phase (gel) in which a solid macromolecule is immersed in a liquid phase (solvent). This is a gelatinous network. Drying the gel by means of low temperature treatments (typically, for example, about 25°C to about 400°C, and more typically about 25°C to about 100°C), results in porous solid matrices (xerogels) which if desired can be calcined into a dense ceramic. With use of rapid drying, aerogels can be made. An important property

of the sol-gel process is that it is possible to generate glass or ceramic material at a temperature close to room temperature.

Direct write nanolithographic printing using sol-gel compositions, including DPN printing, is described in U.S. regular patent application filed December 17, 2002, serial no. 10/320,721, to Mirkin et al., "Patterning of Solid State Features by Direct Write Nanolithographic Printing," which is hereby incorporated by reference in its entirety (now patent publication 2003/0162004 published August 28, 2003).

Patterning of magnetic nanoparticles, and use of magnetic driving forces in patterning, is described in, for example, US Patent Publication 2002/0122873 published September 5, 2003 to Mirkin et al., which is hereby incorporated by reference in its entirety. In a preferred embodiment of this invention, however, magnetic driving forces are not used. Rather, deposition is carried out when the magnetic materials is in a precursor, non-magnetic form. If desired, the magnetic precursor can be chemically linked to the substrate surface, or the substrate can be treated to improve physical binding between ink and substrate.

In the present invention, a variety of methods can be used to form the magnet materials nanostructure. For example, the method can comprise depositing a magnetic material nanostructure precursor on a substrate; and converting the precursor to form the magnetic nanostructure on the substrate. The depositing step can be carried out with use of a solid tip having the magnetic nanostructure precursor at the end of the tip. For example, the depositing step can be carried out with use of a nanoscopic tip or with use of a scanning probe microscope tip. Tips which can function as atomic force microscopic tips (AFM tips) are particularly preferred. In addition, the depositing step can be carried out with use of a hollow tip, wherein the patterning ink is transported through the hollow aspect of the tip. Also, the depositing step can be carried out with use of a sol-gel precursor.

The experimental parameters for nanolithographic printing can be adapted for use in the patterning of magnetic structures including precursors of these structures. During direct write nanolithographic printing, including DPN printing, for example, the contact force can be, for example, between approximately 0.5 nN and approximately 5 nN, more preferably between approximately 1.0 nN and approximately 4 nN, and even more preferably approximately 1.5 and approximately 3.5 nN. In addition, preferably, the humidity is between approximately 20% and approximately 50%, more preferably between approximately 30% and approximately 40%.

The ink composition can be formulated to achieve commercially needed, superior resolution and high quality in the patterned nanostructures. For example, a solvent system can be selected which provides for superior resolution in view of the selected pre-cursor reagents. Basic and novel features of the present invention include that the ink composition is tailored for magnetic printing and does not include components and amounts of components which interfere with this application. The patterning ink composition can consist essentially of components which facilitate magnetic printing applications. For example, solvent selection can be carefully controlled and solvents which do not provide the desired performance at certain concentrations can be excluded. Particulate matter can be excluded, particularly micron scale and larger scale particulate matter in the ink.

Once the magnetic precursor is patterned, the precursor can be converted to a magnetic structure by, for example, heating including both initial pre-heating processes and later stage annealing processes. Preferably, preheating is performed in a temperature range between approximately 350°C and approximately 600°C, more preferably between approximately 400°C and approximately 550°C. Preferably, preheating is performed in a time range between approximately 1 hour and approximately 6 hours, more preferably between approximately 2 hours and approximately 5 hours. Preferably, annealing is

performed in a temperature range between approximately 600°C and approximately 1200°C, more preferably between approximately 700 °C and approximately 1100 °C, most preferably between approximately 800 °C and approximately 1000 °C. Preferably, annealing is performed in a time range between approximately 0.5 hour and approximately 6 hours, more preferably between approximately 1 hour and approximately 5 hours, most preferably between approximately 2 hours and approximately 4 hours.

The nanostructures of interest are generally lateral structures placed on a surface having a height and lateral dimensions other than height such as length and width, particularly if placed in a regular form such as a line or a dot can have a line width or dot diameter. The nanostructure can have a size dimension other than height of about one micron or less. Size dimensions other than height include, for example, lateral measurements such as dot diameters and line widths. Preferably the patterned nanostructure has dimensions between approximately 10 nm to 1000 nm, more preferably between approximately 20 nm to 500 nm, and most preferably between approximately 50 nm to 100 nm. Nanostructures having a size dimension other than height of less than about 100 nm or less, and even less than about 10 nm or less, are of particular interest.

In addition, individual nanostructures can be characterized by their lateral area in square nm. For example, an individual magnetic bar having a length of 100 nm and a width of 100 nm would have a lateral area of 10,000 nm<sup>2</sup>. Individual nanostructures can have, for example, a lateral area of about 100,000 nm<sup>2</sup> or less, more particularly, about 10,000 nm<sup>2</sup> or less, more particularly, about 1,000 nm<sup>2</sup> or less, or more particularly about 100 nm<sup>2</sup> or less.

The height of the nanostructures is not particularly limited and layered structures can be formed. For example, nanostructures having height of about 50 nm or less can be prepared, as well as nanostructures having height less than about 10 nm. Heights of about 5

nm to about 25 nm can be useful. When layered structures are formed, the compositions of the individual layers can be the same or varied.

In general, nanostructures having few individual domains can be made. For example, the number of domains in a nanostructure can be 10 or less, or 5 or less, three, or two.

Arrays of magnetic nanostructures can be prepared in which individual nanostructures can be separated from each other by distances less than about one micron, or more particularly, less than about 500 nm, or more particularly, less than about 100 nm. Another method to characterize separation distance is to measure the distance between the center point of the nanostructure such as the center point of a dot or a center line of a line. The distances between the centers can be, for example, about one micron or less, or more particularly, about 500 nm or less, or more particularly about 100 nm or less. High density patterning can be carried out wherein, for example, a plurality of nanostructures are patterned, optionally in a regular array, and each nanostructure has a small size itself and a small separation distance from an adjacent nanostructure. For example, pattern densities can be one nanostructure per  $5 \times 10^6 \text{ nm}^2$  of substrate area of patterned array or less, or more particularly, one nanostructure per  $5 \times 10^4 \text{ nm}^2$  of substrate area of patterned array or less, or more particularly, one nanostructure per  $5 \times 10^2 \text{ nm}^2$  substrate area of patterned array or less.

The nanostructures can be disposed on a substrate and can be disposed in a mechanically and chemically stable manner. For example, the nanostructures can be sufficiently stable on the substrate to resist solvent washing. If desired, the inks can be formulated and the substrates selected to provide chemical affinity, be it covalent bonding or chemisorption, to the substrate.

The small magnetic structures can be used in a variety of applications including, for example, high-density recording media, nonvolatile memories, microwave circuits,

biosensors, bioelectronics, magnetic microscopy, cell phones, security alarms, and communication devices generally. Magnetic materials can be combined with non-magnetic materials whether in the same deposition structure or separate structures.

Many types of magnetic materials can be used in the present invention, particularly those magnetic materials that can be fabricated using the sol-gel method. Although hard magnetic materials and semi-hard magnetic materials are preferred embodiments of the invention, in another embodiment of this invention, the pattern of magnetic material can comprise soft ferrites, which can be represented by  $\text{MeFe}_2\text{O}_4$ , wherein Me represents a divalent transition metal atom such as, for example, Mn, Zn, Ni, Co, Cu, Fe, and Mg. In particular, Mn-Zn and Ni-Zn ferrite systems can be used. In particular, compositions comprising Mn can be formulated, and manganese ferrite nanostructures and arrays can be made. For example, arrays can be made comprising dots and lines. For dot arrays, the distance from the center of the dots can be, for example, about 50 nm to about 1,000 nm, or more particularly, about 200 nm to about 600 nm. The dot size in diameter can be, for example, about 20 nm diameter to about 1,000 nm, or more particularly, about 50 nm to about 500 nm, and more particularly, about 100 nm to about 250 nm. Line widths can have equal values as dot size diameter, and lines can be as long as desired including over one micron and about one to about 1,000 microns. In general, similar ink compositions can be used for soft and hard magnets except for the selection of metal. Hence, an advantage for this invention is the versatility of the ink system. Soft ferrites can be made by known routes including sintering of mixtures of components comprising the metals.

Semi-hard magnetic materials are described in, for example, U.S. Patent Nos. 3,989,556 to Iwata et al. and 4,695,333 to Inoue et al. Generally, semi-hard magnetic materials are associated in applications more with hard magnetic materials than with soft



magnetic materials. Semi-hard magnetic materials which can be prepared by the sol-gel route are particularly preferred for the present invention.

Inks formulated for preparation of soft ferrites can be formulated from the precursors including metal nitrates or metal acetates and ferric nitrate in appropriate stoichiometric proportions. The solvents can be, for example, ethylene glycol, 2-methoxyethoxyethanol, ethanol, or combinations thereof. When sol gel methods are used, the sol ink can be patterned directly onto surfaces, followed by thermal treatment to cover the sol into the solid phase. Soft magnets can be used in power applications including, for example, transformer cores.

Ceramic magnets can be used including low-conductivity ceramic magnets and superconducting ceramic magnets. Commercial ferrite compositions include metallic ferrites such as, for example, magnesium ferrite, magnesium-zinc ferrite, manganese ferrite, manganese-iron ferrite, nickel ferrite, and lithium ferrite.

In addition, ferrimagnetic materials can be also used. Also, garnets can be used including yttrium iron garnet (YIG), aluminum substituted YIG, chromium substituted YIG, lanthanum iron garnet, and praseodymium iron garnet.

Mixtures of different types magnetic precursors and magnets can be formulated as inks and patterned and converted to final form. In addition, different types of magnetic materials can be patterned and otherwise constructed to form a functional device.

Finally, the invention provides a number of preferred embodiments which are summarized by number:

For example, embodiment 1 is a method of forming a BaFe nanostructure comprising: depositing a BaFe precursor on a substrate via dip pen nanolithographic printing; and heating the precursor to form the BaFe nanostructure on the substrate. Embodiment 2 is the method

of embodiment 1, wherein the substrate comprises Si. Embodiment 3 is the method of embodiment 2, wherein the surface of the substrate comprises SiO<sub>2</sub>. Embodiment 4 is the method of embodiment 1, wherein the step of depositing is performed with a contact force between approximately 0.5 and approximately 5.0 nN. Embodiment 5 is the embodiment of claim 4, wherein the step of depositing is performed with a contact force between approximately 1.0 and approximately 4.0 nN. Embodiment 6 is the method of embodiment 5, wherein the step of depositing is performed with a contact force between approximately 1.5 and approximately 3.5 nN. Embodiment 7 is the method of embodiment 1, wherein the BaFe precursor comprises iron nitrate. Embodiment 8 is the method of embodiment 1, wherein the BaFe precursor comprises barium carbonate. Embodiment 9 is the method of embodiment 1, wherein the BaFe precursor comprises at least one alkylene glycol. Embodiment 10 is the method of embodiment 1, wherein the BaFe precursor comprises ethylene glycol. Embodiment 11 is the method of embodiment 1, wherein the BaFe precursor comprises a solvent which wets the substrate. Embodiment 12 is the method of embodiment 1, wherein the heating step comprises a step of preheating. Embodiment 13 is the method of embodiment 12, wherein the step of preheating is performed in a temperature range between approximately 350 °C and approximately 600 °C. Embodiment 14 is the method of embodiment 13, wherein the step of preheating is performed in a temperature range between approximately 400 °C and approximately 550 °C. Embodiment 15 is the method of embodiment 12, wherein the step of preheating is performed for approximately 1 to 6 approximately hours. Embodiment 16 is the method of embodiment 15, wherein the step of preheating is performed for approximately 2 to approximately 5 hours. Embodiment 17 is the method of embodiment 1, wherein the heating step comprises a step of annealing performed in a temperature range between approximately 600 °C and approximately 1200 °C. Embodiment 18 is the method of embodiment 17, wherein the step of annealing is performed

in a temperature range between approximately 700 °C and approximately 1100 °C.

Embodiment 19 is the method of embodiment 18, wherein the step of annealing is performed in a temperature range between approximately 800 °C and 1000 °C. Embodiment 20 is the method of embodiment 17, wherein the step of annealing is performed for approximately 0.5 to approximately 6 hours. Embodiment 21 is the method of embodiment 20, wherein the step of annealing is performed for approximately 1 to approximately 5 hours. Embodiment 22 is the method of embodiment 21, wherein the step of annealing is performed for approximately 2 to approximately 4 hours. Embodiment 23 is the method of embodiment 1, wherein the nanostructure is magnetic. Embodiment 24 is the method of embodiment 1, further comprising the step of sonicating the precursor solution before deposition. Embodiment 25 is the method of embodiment 1, wherein the step of depositing comprises a step of dipping an AFM tip into a precursor solution. Embodiment 26 is the method of embodiment 1, wherein the nanostructures range from approximately 10 nm to approximately 1000 nm. Embodiment 27 is the method of embodiment 26, wherein the nanostructures range from approximately 20 nm to approximately 500 nm. Embodiment 28 is the method of embodiment 27, wherein the nanostructures range from approximately 50 nm to approximately 100 nm. Embodiment 29 is the method of embodiment 1, wherein the nanostructures are in the form of lines having line width of about 10 nm to about 1000 nm. Embodiment 30 is the method of embodiment 1, wherein the nanostructures are in the form of lines having line width of about 20 nm to about 500 nm. Embodiment 31 is the method of embodiment 1, wherein the nanostructures are in the form of lines having line width of about 50 nm to about 100 nm. Embodiment 32 is an array comprising nanostructured BaFe. Embodiment 33 is an array comprising nanostructured BaFe prepared by dip pen nanolithographic printing. Embodiment 34 is an array comprising dots of nanostructured BaFe prepared by dip pen nanolithographic printing and having a mean diameter of about 35 nm. Embodiment 35 is an array comprising lines of

nanostructured BaFe prepared by dip pen nanolithographic printing and having line widths of about 10 nm to about 1,000 nm. Embodiment 36 is an array prepared by the method of embodiment 1. Embodiment 37 is an array comprising bars of BaFe prepared by dip pen nanolithographic printing, wherein the bars have an average area of about  $215 \times 465 \text{ nm}^2$  and an average height of about 7 nm. Embodiment 38 is an array comprising bars of BaFe prepared by dip pen nanolithographic printing, wherein the bars have an average average height of about 5 nm to about 25 nm. Embodiment 39 is an array comprising bars of BaFe prepared by dip pen nanolithographic printing, wherein the bars have an average average height of less than about 15 nm. Embodiment 40 is a method of forming a BaFe nanostructure consisting essentially of: depositing a BaFe precursor on a substrate via dip pen nanolithographic printing; and heating the precursor to form the BaFe nanostructure on the substrate. Embodiment 41 is an information storage system comprising BaFe nanostructures manufactured by the process of embodiment 1. Embodiment 42 is an information storage system of embodiment 41, wherein the information density is greater than approximately 60 Gb/in<sup>2</sup>. Embodiment 43 is a method of embodiment 1, wherein the step of depositing is performed with a humidity between approximately 20% and approximately 50%. Embodiment 44 is the method of embodiment 43, wherein the humidity is between approximately 30% and approximately 40%.

The present invention is not limited by the specific embodiments expressly disclosed herein.

## WORKING EXAMPLES

The invention is further described by means of the following nonlimiting working examples.

BaFe nanostructures on a silicon oxide substrate were generated according to the following procedure. The surface of a SiO<sub>2</sub>/Si wafer was first patterned via nanolithographic printing (contact force 2.5 nN; humidity 31 %; temperature 24 °C) using an atomic force microscope (AFM) cantilever coated with a BaFe precursor solution that contains a mixture of iron nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and barium carbonate (BaCO<sub>3</sub>) in ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH). The ethylene glycol dissolves and stabilizes the starting materials; it also wets the hydroxylated substrate, a factor that is important in the nanopatterning process. Indeed, ethylene glycol surprisingly provided better results not readily obtainable by 2-propanol, water, methanol, or ethanol as the solvents under nearly identical conditions. For example, some selection of solvents resulted in quick evaporation and immediate drying of the ink, and other selection of solvents resulted in excessive stickiness making patterning difficult. The patterns were preheated at 450 °C for 4 h and then annealed at 950 °C in an air atmosphere for 2 h, ultimately yielding BaFe nanostructures (Fig. 1).

In order to compare the chemical and structural properties of the nanostructures with BaFe, bulk samples of BaFe particles and films were prepared by the aforementioned sol-gel method. The x-ray diffraction (XRD) pattern of the as-synthesized BaFe particles showed a series of Bragg reflections that can be well indexed as M-type hexagonal BaFe (Fig. 2a). In contrast, the XRD pattern of the sample without preheating showed peaks corresponding to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase (Fig. 2b). The size, morphology, and crystal structure of the BaFe particles were also investigated with a HF-2000 field emission gun (FEG) transmission electron microscope (TEM). The polygonal particles have a mean diameter of ~35 nm (Fig. 2c). High resolution TEM showed the lattice image of a BaFe particle viewed along the [110]<sub>c</sub> projection (Fig. 2d). Elemental analysis, using energy-dispersive x-ray spectroscopy (EDS) operating in the STEM mode, confirmed the presence of Ba, Fe, and O in individual

nanoparticles as well as aggregate structures (Fig. 2e). The magnetic properties of the BaFe nanoparticles were investigated at room temperature by superconducting quantum interference device magnetometry (SQUID). The magnetic nanoparticles exhibit a "squarish" hysteresis loop with a high coercivity (4250 Gauss) and a large remnant magnetization (32.2 emu/g), which is consistent with earlier reports on BaFe particles (Fig. 2f) (see documents 15 and 16).

In a typical nanopatterning experiment, the BaFe precursor solution in ethylene glycol was prepared (see Methods section) and sonicated for 15 min before being used. A silicon nitride AFM micro cantilever was then dipped into the solution for 1 min. The cantilever was blown dry with compressed difluoroethane to obtain proper laser reflecting alignment. The barium ferrite precursor solution was deposited on a SiO<sub>2</sub>/Si substrate by bringing the coated AFM tip in contact with the surface and then moving it across the substrate, using nanolithography software (available, Nanolnk, Inc.,<sup>TM</sup> Chicago, IL). The aforementioned post-treatment procedure was used to generate all patterns reported herein (Fig. 3). With this strategy, magnetic nanostructures with dimensions ranging from several hundred nanometers down to 90 nm were generated.

When a magnetic material is patterned into arrays in the form of nanosized dots, bars, or columns on a nonmagnetic matrix, each feature contains one or, at most, a few domains in contrast to the multidomain structure of conventional storage medium (for example, magnetic thin films) (see document 14). The patterned media in such structures remain stable down to much lower lateral dimensions than conventional bits in continuous media (see document 14). Lines of BaFe with an average width of 90 nm were generated via the combined DPN printing sol-gel approach (Fig. 3a). Arrays of magnetic BaFe bars that have an average area of 215 X 465 nm<sup>2</sup> with an average height of 6.7 nm were also generated by controlling the tip-substrate scan speed (Fig. 3b, c). Preferably, the magnetic bars have an average height of

about 5-25 nm. The magnetic properties of the nanopatterns were further examined by magnetic force microscopy (MFM) in lift mode. Before imaging, the tip, coated with a ferromagnetic thin film of cobalt, was magnetized with an external magnetic field. The magnetic force was then detected by measuring the phase shift in the cantilever oscillation, a consequence of the magnetic interactions acting on the tip. The MFM image indicates that these patterns were indeed magnetic (Fig. 3d). The elemental composition of the magnetic nanostructures on the substrate was determined by x-ray photoelectron spectroscopy (XPS). The  $\text{Ba}3d_{5/2}$ , and  $\text{Ba}3d_{3/2}$  peaks were observed at 780.6 eV and 795.9 eV, respectively, which were the characteristic values for  $\text{BaFe}_{12}\text{O}_{19}$  (Fig. 3e). The  $\text{Fe}2p_{3/2}$  and  $\text{Fe}2p_{1/2}$  peaks were observed at 710.9 eV and 724.5 eV respectively, which were diagnostic of BaFe (Fig. 3f). The O1s spectrum showed a large FWHM of 2.5 eV, which was broadened on the low binding-energy side (Fig. 3f(inset)). The O1s spectrum could be resolved into two peaks using a least-square curve fitting method with a mixture of Gaussian and Lorentzian functions on a Shirley-type background (see document 26). The low binding-energy peak at 530.4 eV represents the  $\text{O}^{2-}$  contribution in the  $\text{BaFe}_{12}\text{O}_{19}$  while the peak at high binding-energy of 533.3 eV is attributed to the  $\text{OH}^-$  on hydroxylated surface of silicon dioxide (see document 27).

## Methods

### Particle synthesis and Substrate preparation

Iron nitrate (4 g; 0.0115 mol) and barium carbonate (0.197 g; 0.001 mol) were dissolved in a solution of ethylene glycol (25 mL). Silicon oxide wafers were cleaved into two 0.5 in. X 0.5 in. squares and sonicated in dichloromethane, methanol, and Nanopure water for 10 min, respectively. The wafers were then immersed in freshly mixed ammonium hydroxide/peroxide solution ( $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ , v:v:v = 1:1:5) for 1 hour at about 100°C,

after which time they were rinsed in Nanopure water. The wafers were dried in nitrogen gas before immersion in the different solvents.

#### Characterization of the BaFe

XRD spectra were recorded using a Rigaku X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation operated at 45 kV and 20 mA. The diffraction angles were referenced to those for high-purity Si powder. The size and morphology of the particles were determined with a HF-2000 field TEM (Hitachi, Japan). The size distribution was determined by measuring the diameters of 400 particles. Magnetic measurements were performed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS). XPS spectra were recorded using an Omicron ESCA probe operated in vacuum at around  $4.8 \times 10^{-10}$  torr with monochromated Al K $\alpha$  radiation (1486.6 eV, 300 W). Binding energies were corrected by referencing the C1S signal of adventitious hydrocarbon to 284.8 eV. The electron-pass energy in the analyzer was set at 50 eV.

#### AFM and MFM

Direct write nanolithographic printing experiments were carried out under ambient conditions (31 % relative humidity and 24°C) with a Thermomicroscopes CP AFM and commercial cantilevers (force constant = 0.05 N/m, Si<sub>3</sub>N<sub>4</sub>). To minimize piezo tube drift problems, a 90- $\mu$ m scanner with closed loop scan control was used for all of the DPN printing experiments. AFM and MFM measurements were made in air using a Digital Instruments Multimode Nanoscope IIIa with an extender electronics module in tapping and lift modes, respectively.

Finally, Figure 4 illustrates a working example for manganese ferrite arrays printed by DPN patterning, as imaged by AFM, using procedures described above for barium ferrite. In



Figure 4, the dot size was about 150 nm, and the distance between the center of the dots was about 400 nm. Ink formulation was the same as for the barium ferrite, however, manganese nitrate and ferric nitrate were used in ethylene glycol. The same results were found with manganese acetate used as the Mn source. Silicon and silica substrates provided excellent printing results.

In summary, the working examples have shown construction of barium ferrite and manganese ferrite nanostructures, based on a combination of a novel sol-gel process and the direct write nanolithographic printing method. The combined approach, which takes into account the versatility and attributes of direct write nanolithographic printing (direct-writing, feature shape and size control, and soft matter compatibility), provides for constructing sophisticated architectures of magnetic, ceramic, and conductive nanostructures that can provide further insight into magneto-electronic sensor devices and high density information storage systems. Indeed, based on the feature size attainable via this approach, performance can be found at a density of greater 60 Gb/in<sup>2</sup>. Parallelization of nanolithographic printing can be used in achieving this density (see, for example, document 28).

The following documents, which are not admitted prior art, can further enable one to practice the present invention.

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All of the documents above, 1-64, are incorporated by reference in their entirety. Multiple embodiments are disclosed in this provisional application for fabricating magnetic patterns with use of dip pen nanolithographic printing as a patterning tool. For all embodiments in this disclosure, documents 17-24, 28-55 and 63 above, which relate to dip pen nanolithographic printing methods, are hereby incorporated by reference in their entirety and form part of the present disclosure. Further, documents 1-10, which relate to magnetic nanoscale materials exhibiting novel size-dependent properties are also hereby incorporated by reference in their entirety. In addition, documents 11-14, which relate that magnetic nanoscale materials are being explored as potential avenues to high-density recording media, are also hereby incorporated by reference in their entirety. Documents 15 and 16 relate that barium hexa-ferrite (BaFe), in particular, is a good hard magnet candidate for such media and are hereby incorporated by reference in their entirety. Documents 25, 56-59 and 64 relate to sol-gel processes for forming metal oxides and are hereby incorporated by reference in their entirety. Documents 26 and 27 relate to x-ray photoelectron spectroscopy analysis; document 60 relates to making carbon nanotubes; document 61 relates to making mesostructural waveguides; and document 62 relates to making nanocomposites; all of which are hereby incorporated by reference in their entirety.